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<b>13. SUPPLEMENTARY NOTES</b>					
<b>14. ABSTRACT</b> Organic diradicals, in which the atomic orbitals carrying spin density, have near-perfect alignment for strong ferromagnetic exchange coupling, were designed, synthesized, and characterized by magnetic studies. These include novel triplet ( $S = 1$ ) ground state aminyl diradicals, in which spin density is centered at nitrogen atoms, and $S = 1$ ground state nitroxide diradicals, in which spin density is primarily located at nitrogen and oxygen atoms. The nitroxide diradicals are stable at ambient conditions. These diradicals were intended as ligands (monomers) in ferrimagnetic coordination polymers magneto-dielectric properties.					
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# FINAL REPORT

## Technical Section

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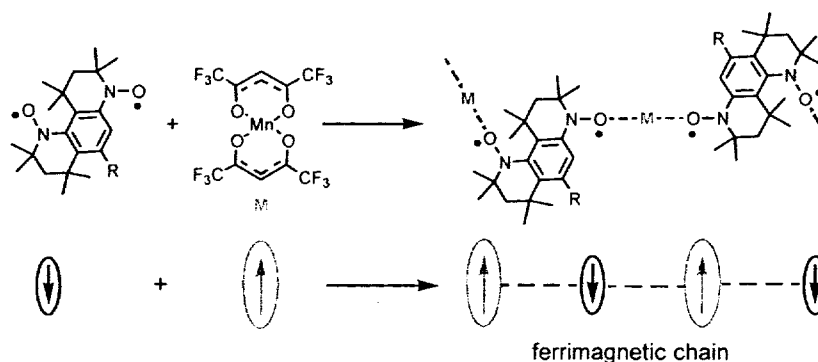
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### Technical Objectives

The primary objective of this project is the development of materials that are both soft magnets and soft dielectrics (with comparable values of permittivity and magnetic permeability) in the GHz-frequency range. Such materials would enable novel approach to high performance RF antennas. This combination of properties is difficult to attain in conventional magneto-dielectric materials; especially, obtaining soft properties (low loss) in the GHz-frequency range is a challenge.

### Technical Approach

Our approach relies on ferrimagnetic coordination polymers, consisting of Lewis basic organic di- and polyradicals and Lewis acidic paramagnetic transition metal ions (Figure 1). Selection of metal ions (e.g., Mn(II) with half-filled d-levels) and intrinsic properties of organic radicals (light nuclei, short conjugation lengths) is compatible with soft magnetic and dielectric properties. The key problem is that the magnetic ordering temperatures for such coordination polymers (polymer networks) are limited by the strength of the ferromagnetic exchange coupling within the organic diradical or polyradical. To address this problem, we designed and developed synthetic methodology for Lewis basic, planarized organic diradicals, in which the 2p-orbitals, carrying spin density, have near-perfect parallel alignment.

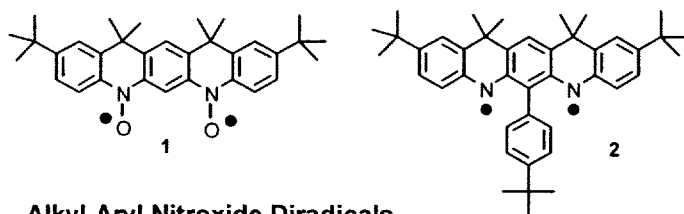


**Figure 1.** Proposed approach to ferrimagnetic polymers based upon polymerization of Lewis basic planarized nitroxide diradicals with Lewis acidic transition metal ion complexes.

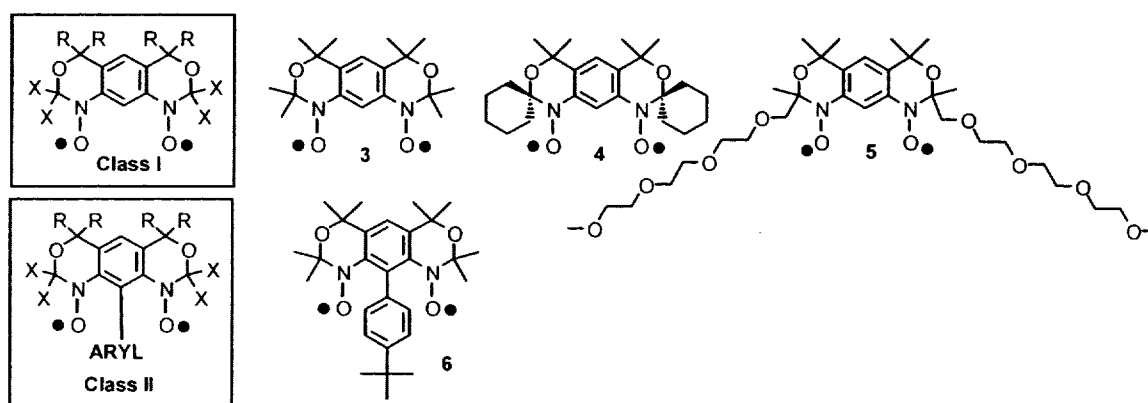
## Results

Research publications resulting from the AFOSR support are listed in the references.<sup>1-9</sup> Aminyl and nitroxide diradicals, which were prepared and fully characterized, are summarized in Figure 2. Unpublished work and the key aspects of synthesis and characterization of diradicals, as well as attempts at polymerization of diradicals with transition metal complexes, are described below.

### Aryl-Aryl Nitroxide Diradical and Aminyl Diradical

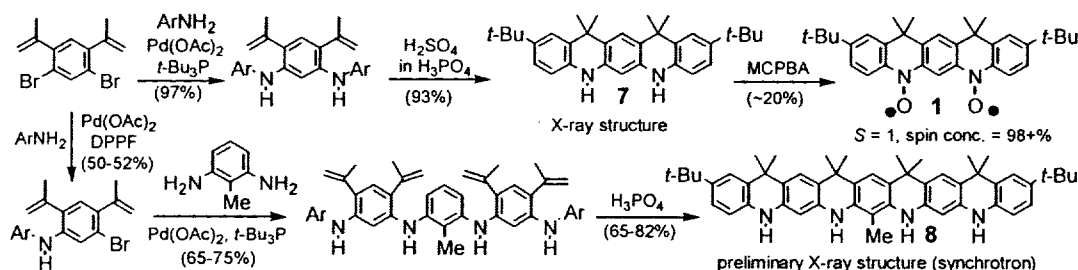


### Alkyl-Aryl Nitroxide Diradicals



**Figure 2.** Summary of prepared and characterized triplet ( $S = 1$ ) ground state nitroxide and aminyl diradicals.

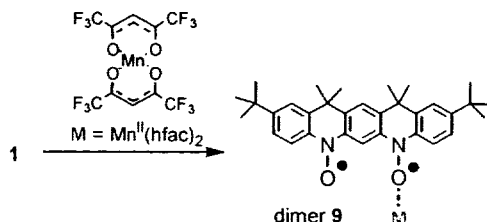
The design and synthesis of diaryl nitroxide diradicals, in which both nitroxide moieties are flanked by aryl rings, could enable synthesis of high-spin  $S > 1$  polyradicals. (Such polyradicals could enable preparation of coordination polymers with transition metal ions of higher dimensionality.) We prepared the first such diaryl nitroxide diradical **1** (Figure 3); **1** is stable at ambient conditions and it possesses  $S = 1$  ground state with large singlet-triplet energy gap both in the solid state ( $2J/k \gg 300$  K) and in solution ( $2J/k > 200$  K). EPR studies of **1** showed well-resolved  $^{14}\text{N}$ -hyperfine coupling with the  $|A_{yy}/2hc|$  splitting, indicating that the nitroxides are coplanar with *m*-phenylene.<sup>8</sup>



**Figure 3.** Synthesis of diradical **1**, diamine **7**, and tetraamine **8**. Ar = 4-*tert*-butylphenyl.

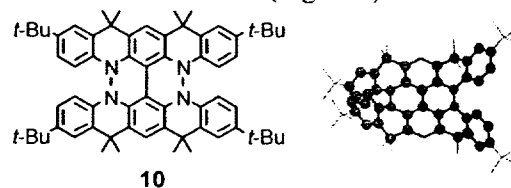
This synthetic methodology developed for diamine **7** was extended to tetraamine **8**, via tetra-connection and tetra-annulation steps (Figure 3). With the blocking group, such as methyl, at the *ortho* position, tetraamine **8**, with nine co-linearly annelated rings, is obtained in high yield. Oxidation of **8** with MCPBA gave  $S = \frac{1}{2} - 1$ ; screening for optimum routes to the tetraradical is in progress.

Polymerization of diradical **1** with  $\text{Mn}(\text{hfac})_2$  yielded only dimeric products, which were characterized magnetically and assigned structure **9** (Figure 4).



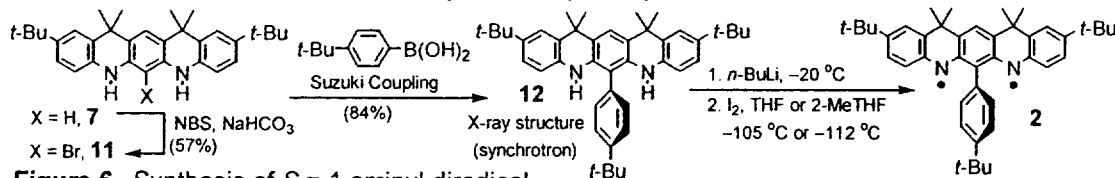
**Figure 4.** Attempted polymerization of diradical **1**.

In the process of optimization of synthesis of nitroxide diradical **1** via oxidation of diamine **7**, we discovered a novel  $\pi$ -conjugated chiral system, conjoined double helicene **10**, in which two molecular helices are fused in their midsections (Figure 5).<sup>1,3,4</sup>



**Figure 5.** Structure drawing of conjoined double helicene **10** and the actual structure as obtained by the X-ray crystallography. Each of the two molecular helices is shown in stick-and-ball.

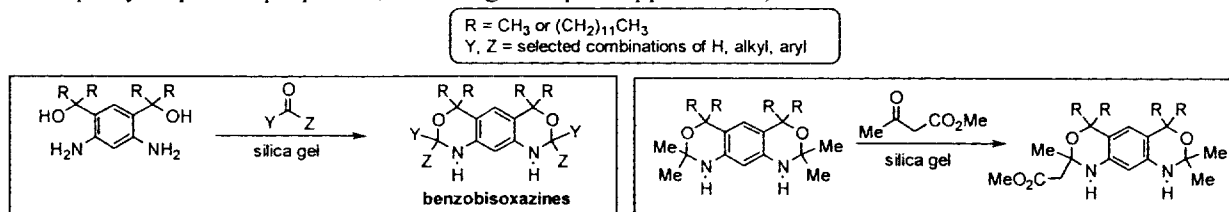
Efficient methodology for generation of aminyl diradicals, as illustrated for diradical **2**, was developed (Figure 6).<sup>7</sup> Starting from diamine **7** and tetraamine **8**, this methodology gave aminyl radicals with  $S = \frac{1}{2}$  and  $S = 1$ , respectively. However, starting from diamine **12**, in which the center *ortho*-position was sterically shielded with 4-*tert*-butylphenyl by the sequence of bromination and Suzuki coupling,  $S = 1$  aminyl diradical **2** was cleanly obtained (Figure 6). The magnetic studies and EPR spectroscopy show  $S = 1$  ground state with  $2J/k > 200$  K and co-planar diarylaminyis.<sup>7</sup>



**Figure 6.** Synthesis of  $S = 1$  aminyl diradical.

As planarized planarized aryl-aryl nitroxide diradical **1** could not be polymerized with Lewis acidic  $\text{Mn}^{\text{II}}$ -based complexes (Figure 4), we developed synthetic approaches to stable alkyl-aryl nitroxides, which should be a stronger Lewis bases than **1**. This approach is based upon the first general and efficient method for preparation of benzobisoxazines (Figure 7).<sup>5</sup> Benzobisoxazines are not only the selected precursors for the corresponding nitroxide diradicals (Figure 2), but they may provide monomers for another type of polybenzoxazines. (Typical polybenzoxazines, derived from 3,4-dihydro-2H-1,3-

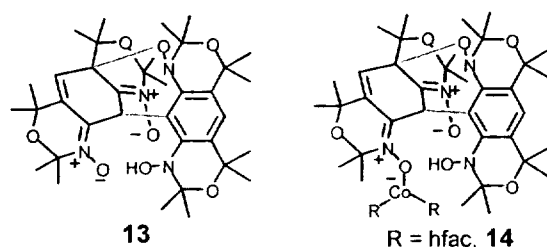
benzoxazines, are thermosetting resins for polymer composites with superior mechanical, flame-retardant, and superhydrophobic properties, including aerospace applications.)



**Figure 7.** Synthesis of benzobisoxazines by silica gel catalysis.

Oxidation of benzobisoxazines produced corresponding nitroxide diradicals **3**, **4**, and **5** (Figure 2) in good yields and with high purities.<sup>6,9</sup> Diradical **3** is planar (X-ray crystallography). Diradicals **3**, **4**, and **5** possess  $S = 1$  ground state with large singlet triplet gap both in the solid state ( $2J/k \gg 300$  K) and in solution ( $2J/k > 200$  K). Diradical **5** was recently employed as one of the model compounds to probe electron spin relaxation properties of organic diradicals and polyradicals.<sup>9</sup>

Polymerizations of diradical **3** with transition metal ions,  $\text{Mn}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ , and  $\text{Ni}^{\text{II}}$ , resulted in isolation of low molecular weight materials only. For example, polymerization of dinitroxide **4** with  $\text{Mn}^{\text{II}}(\text{hfac})_2$  and  $\text{Co}^{\text{II}}(\text{hfac})_2$  led to isolation of compounds **13** and **14** (Figure 8). Structures of compounds **13** and **14** were unequivocally determined by X-ray crystallography.<sup>6</sup>



**Figure 8.** Structures of compounds **13** and **14** as characterized by X-ray crystallography. Molecule of water complexed to cobalt in **14** is omitted for clarity.

Structures of **13** and **14** may be considered as dimers of nitroxide diradical **3**, in which two molecules of **3** are connected via C-C and C-O bonds (red lines in Figure 8). The formation of C-C bond, between the two *ortho*-positions with respect to radicals, was especially surprising. Therefore, we developed synthesis of nitroxide diradical **6**, in which the *ortho*-position is blocked by the bulky 4-*tert*-butylphenyl group, to prevent the dimerization (Figure 2).<sup>6</sup>

Although, X-ray structure of **6** indicated that the nitroxides were slightly bent out-of-the-plane of the *m*-phenylene, magnetic studies showed that **6** possesses  $S = 1$  ground state with a substantial  $2J/k \geq 500$  K. ( $2J/k$  in this range is difficult to measure accurately.) These experimental results are consistent with the UB3LYP/6-31G\* calculations:  $2J/k = 1600$  K (3.3 kcal/mol) for **3** and  $2J/k = +1100$  K (2.2 kcal/mol) for **6**.<sup>6</sup>

Detailed magnetic and structural studies revealed that crystalline diradicals **3** and **6** form unprecedented examples of organic one-dimensional, highly isotropic antiferromagnetic chains, with intra-chain antiferromagnetic coupling between  $S = 1$  diradicals,  $2J_{\text{CHAIN}}/k = -7$  K and  $-4$  K, mediated through C-H...O non-classical hydrogen bonds.<sup>6</sup> Such one-dimensional, isotropic, antiferromagnetically coupled with integer local spins (e.g.  $S = 1$ ) are of fundamental interest in the recent area of spin quantum liquids.

## Conclusion

Synthetic methodologies for novel planarized  $S = 1$  nitroxide diradicals and aminyl diradicals are developed. Such diradicals are found to possess triplet ( $S = 1$ ) ground states with large singlet-triplet energy gaps. For nitroxide diradicals, which are stable at ambient conditions, population of the singlet excited states is not detectable at room temperature, i.e., the measured singlet-triplet gaps far exceed thermal energy at room temperature. Our attempts to use such planarized nitroxide diradicals as monomers for coordination polymers with transition metal complexes led only to isolation of low molecular weight materials.

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2. A. Rajca, "The physical organic chemistry of very high-spin polyradicals." *Adv. Phys. Org. Chem.*, Eds. J. P. Richards, T. Tidwell, **2005**, *40*, 153 – 199.
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4. A. Rajca, S. Rajca, M. Pink, M. Miyasaka, "Annelated, Chiral  $\pi$ -Conjugated Systems: Tetraphenylenes and Helical  $\beta$ -Oligothiophenes" *Synlett*, invited account, submitted.
5. G. Spagnol, A. Rajca, S. Rajca, "Efficient Synthesis of Tricyclic Benzobisoxazines by Silica Gel Catalysis" *J. Org. Chem.* **2007**, *72*, 1867 – 1869.
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7. A. Rajca, K. Shiraishi, M. Pink, S. Rajca, "Triplet ( $S = 1$ ) Ground State Aminyl Diradical," *J. Am. Chem. Soc.*, submitted.
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9. H. Sato, V. Kathirvelu, G. Spagnol, S. Rajca, A. Rajca, S. S. Eaton, G. R. Eaton "Electron spin relaxation of nitroxide diradicals and tetradical in glassy solvents between 10 and 300 K," manuscript in preparation.

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